

# New Aspects of Polyamide 6 Mixing in Molten State with Low-Density Polyethylene

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**ABSTRACT:** A static mixer assembled on a Brabender plastograph has been used as a blender of immiscible polymers like low-density polyethylene (LDPE) and polyamide 6 (PA6). The shearing rates were 50 and 100 s<sup>-1</sup>. The properties of polymer blends were tested using a thermomechanical method. It was found that a tested prototype static mixer imparted good uniformity to the blends' structure on a level similar to molecular distribution of components. This phenomenon is called mechanical compatibilization. High effectiveness of mixing was observed for LDPE-PA6 compositions with and without a compatibilizer. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1807-1811, 1997

**Key words:** mechanical compatibilization; static mixer; pseudomolecular distribution; PA6; LDPE; thermomechanical method

## INTRODUCTION

It is well known that properties of multicomponent polymer composites depend on dispersion, degree of dispersed phases, and related border surface area. Obtaining fine and stable dispersion of components immiscible at compounding temperature is difficult. To increase the dispersion, many different machines or attachments to processing machines are used.<sup>1-8</sup> One of them, for molten polymers, has been tested in this study. A thermomechanical method was used to evaluate the changes in a composite's structure during mixing.

### Testing Methodology

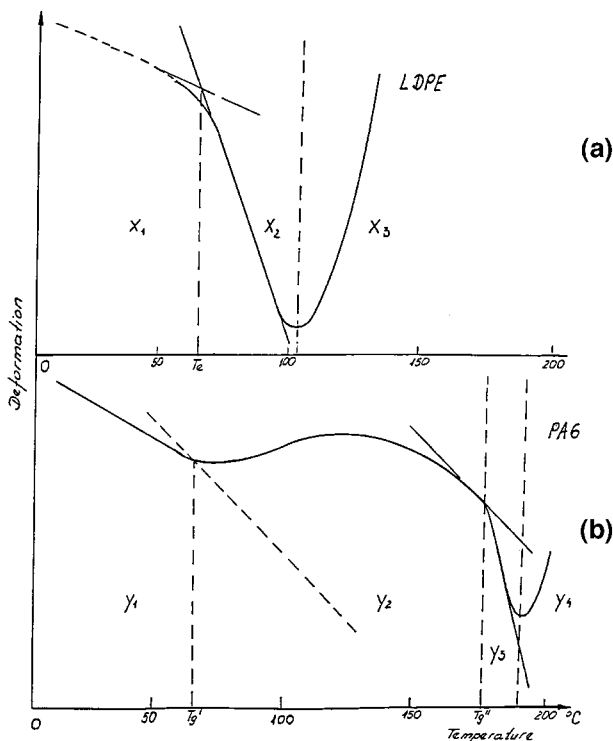
Polymers or their composites were cut to form cylindrical tablets 2-6 mm in diameter and 1-6

mm in thickness. The samples were placed in the heating chamber of thermomechanical device UIP-70M made by the Russian Academy of Sciences to be frozen without pressing under a scanning rate of 2-10°C/min to a temperature of -100°C. Next, the samples were stored for 10-15 min to stabilize temperature. A quartz sonde (Fig. 1) with a tip having a 2-mm radius was used to press a sample with a load of 200 mg. The sonde was moved down to contact a sample's surface, and the sample was defrosted at a rate of 5°C/min. This rate of heating (between 1 and 5°C/min) does not significantly influence the characteristics of the studied processes in polymers when the sample is heated from -100°C to over the melting temperature. By use of a two-axis coordinate recorder (deformation-temperature), a full thermomechanical curve (TMC) was recorded. In this study, a resultant of thermal expansion, thermomechanical and molecular flow of the sample, is understood as deformation. An example of the calculation used was given in our previous article.<sup>9</sup>

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**Figure 1** Typical thermomechanical curves of (a) LDPE and (b) PA6; ( $X_1$ ) transitional zone of solid state of LDPE (mixture of glassy and high-elastic states); ( $X_2$ ) zone of the high-elastic state of LDPE; ( $X_3$ ) zone of molecular flow of LDPE; ( $Y_1$ ) zone of glassy state of PA6; ( $Y_2$ ) zone of high-elastic state of a low-temperature phase of PA6; ( $Y_3$ ) zone of high-elastic state of a high-temperature phase of PA6; ( $Y_4$ ) zone of molecular flow of PA6.

## EXPERIMENTAL

### Characteristics of Materials

The TMCs of individual polymers used in this study are shown in Figure 1. It is evident [Fig. 1(a)] that the temperature range of 60–75°C defines a transitional zone of thermal high-elastic expansion of low-density polyethylene (LDPE) macromolecules. Molecular flow of amorphous LDPE starts at a temperature of about 100°C.

The initial thermomechanical curve of polyamide 6 (PA6) is shown in Figure 1(b). The shape of the curve is typical of diblock (two-phase) material. Here the block is understood as a fraction of the polymer containing different chemical or topological arrangements of chains. In this case, a high-temperature block of PA6 can be seen to have a pseudocrystalline arrangement, with “knots” of branching for a low-temperature block.

This low-temperature block has a pseudocross-linked structure. A low-temperature phase with a glass transition temperature  $T_g$  of about 60°C ends to be visible on the TMC at a temperature of about 150°C by transition to a plateau of high elasticity. The structure of chains in this phase is more ordered than that of a low-temperature phase. This ensures a pseudocrystalline supermolecular arrangement of a high-temperature phase characterized by a  $T_g$  of about 170°C and a zone of molecular flow starting at 200°C. The weight share of a low-temperature phase is about 80–90% of the polymer content.

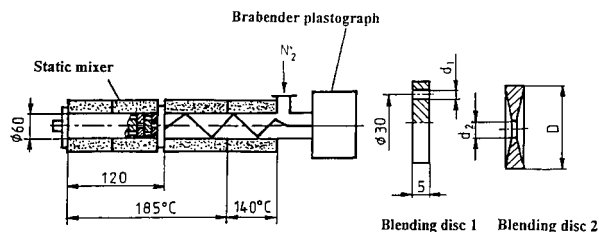
In some experiments, block copolymer styrene-(ethylene butylene)styrene (SEBS) was used as a compatibilizer of the PA6–LDPE blend. The structure of SEBS will be described later.

### Mixing Conditions

Polymers were mixed using laboratory equipment based on a modified Brabender plastograph (Figure 2).<sup>2–8</sup> A static mixer was attached to the extruder of the plastograph to allow components to be mixed under controlled conditions. The mixer permits shearing rates of 50 or 100  $s^{-1}$  to be applied. For the shearing rate of 50  $s^{-1}$  mixing discs were used having 12 holes of  $d_1 = 1.2$  mm, whereas for the shearing rate of 100  $s^{-1}$ , 24 holes of  $d_1 = 0.9$  mm were made. The central hole of  $d_2 = 5$  mm was drilled in the No. 2 discs. Discs Nos. 1 and 2 have an outer diameter  $d = 39$  mm. Their thicknesses are 4 and 5 mm, respectively. The length of the static mixer in which discs Nos. 1 and 2 alternated is 120 mm. The rates at which the molten batch was moved through the static mixer were so selected that the mixture was exposed about 4 min to the regions heated up to 185°C.

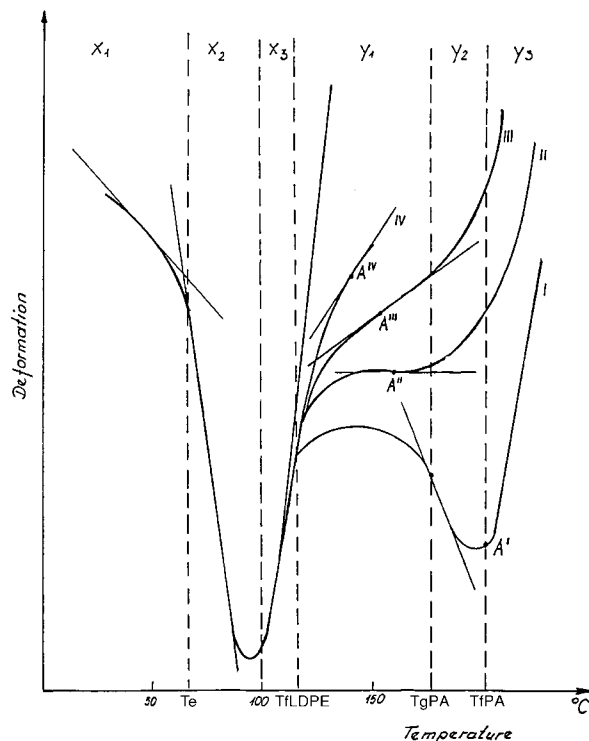
### Mixing LDPE With 5% PA6

Obtaining a uniform composition by mixing a small amount of one component in a matrix of the



**Figure 2** Static mixer design.

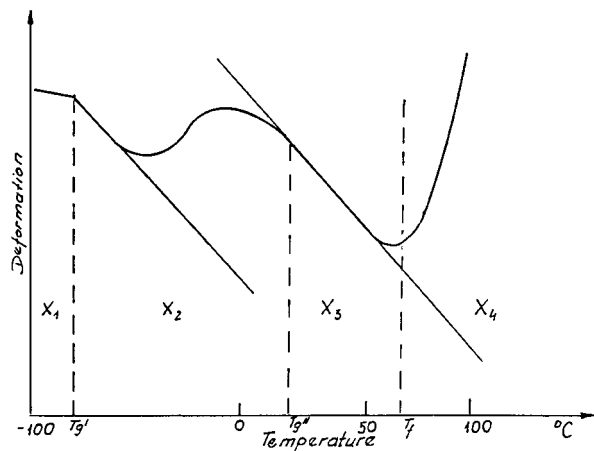
second one (an admixture) is a difficult problem, especially if the components are immiscible. Different numbers of passes through our prototype mixer were used to study the effectiveness of mixing. After the first cycle (the first pass through the extruder and the static mixer) discussed in a previous work<sup>10</sup> (when microscopic observations of the morphological structures of blends at  $250\times$  magnification were made and roughness of sample surface, viscosity, and water adsorption were measured), it was found that the static mixer used in the study significantly improved homogeneity of blends of thermodynamically immiscible polymers. The particles of a dispersed phase obtained were fine with increasingly high border surface areas after every successive pass. The mixer helped to stabilize the blend's morphology after cooling. Additional information about the reason for compatibilization during processing with a static mixer can be obtained through a thermomechanical method. In the present study, it was observed that PA6 is nonuniformly distributed in a matrix of LDPE. Most of the admixtures are concentrated in microdomains with a share of PA6 much greater than 5%. How much greater? Answering now is difficult because extracting PA6 from a small sample of the batch (about  $1\text{ mm}^3$ ) is impossible with sufficient accuracy. As a result, most of the LDPE matrix volume does not contain an admixture of PA6 at all or contains only a small quantity of the admixture (much below 5%). Thus, the influence of PA6 on the thermomechanical curve is on the level of resolution of the device used. Because of this, after the first pass through the mixer, it was found on the basis of 10 parallel experiments that pure LDPE was evident from the TMC only in 8 cases (i.e., no PA6 characteristic peaks were present). A clear PA6 component of this curve was found only in two cases. This finding is illustrated in Figure 3 (curve I). We expected that the concentration of PA6 in LDPE in this sample would be much more than 5%. On this basis all stages from solid state to molecular flow of every component are presented in the TMC. The different influences of the LDPE and PA6 components on the shape of the thermomechanical curve are also evident. The curve indicates that this blend has the structure of block polymers (two-phase systems). The location of the PA6 phase is practically the same as for pure PA6 (Fig. 1), but the zone of the glassy state characteristic of the low-temperature phase disappears. This finding discloses that the polyamide became a single-phase material after the first



**Figure 3** Combined thermomechanical curves of LDPE-PA6 blend passed through the static mixer attached to the extruder of Brabender's plastograph; ( $X_1$ ) zone of solid state of LDPE; ( $X_2$ ) zone of high-elastic state of LDPE; ( $X_3$ ) zone of molecular flow of LDPE; ( $Y_1$ ) zone of glassy state of PA6; ( $Y_2$ ) zone of high-elastic state of PA6; ( $Y_3$ ) zone of molecular flow of PA6; (I-IV) numbers of passes. Te: beginning of elastic deformation of LDPE; TILDPE: beginning of molecular flow of LDPE; TgPA: glass transition temperature of PA; TIPA: beginning of molecular flow of PA.

pass of the batch through the static mixer. This and further passes of the blend through the mixer did not change the structure of the LDPE phase.

After the second and remaining successive cycles of mixing, the number of microdomains with a concentration of PA6 related to that shown in Figure 3 (curve I) gradually decreased. After the second cycle of mixing, in 3 or 4 of the 10 experiments the TMC evidences samples containing more than 5% PA6, but less than the amount shown in Figure 3 (curve I). In the remaining 6 or 7 cases, TMCs characteristic of a blend containing very little or no PA6 were obtained. In the PA6 phase, as a result of the second stage of mixing, a confluence of glassy and high-elastic zones is observed. Simultaneously, the temperature at the beginning of a flow of this phase is reduced by  $20\text{--}30^\circ\text{C}$  (curve A''B'' in Fig. 3).



**Figure 4** Typical thermomechanical curve of SEBS; ( $X_1$ ) zone of solid state of the first phase; ( $X_2$ ) zone of high-elastic state of the first phase and the glassy state of the second phase; ( $X_3$ ) zone of high-elastic state of the second phase; ( $X_4$ ) zone of molecular flow of SEBS.

The third cycle of mixing yielded an improvement in composition uniformity. Here, in 7 or 8 of the 10 experiments, the TMC in the zone characteristic for PA6 is a bit lower than that for the 5% concentration of PA6. This case is illustrated in Figure 3 (curve III). In 2 or 3 cases, TMCs characteristic for a blend containing very little or no PA6 were obtained. Simultaneously, a more pronounced glassy state with a high-elastic state of PA6 and a temperature reduction of 10–20°C at the beginning of a flow of this phase ( $T_g''$  at about 160°C) are observed.

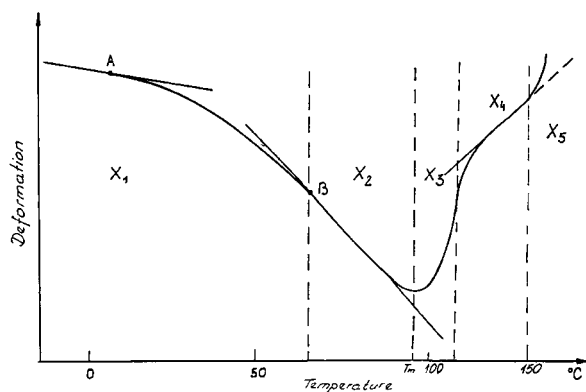
The fourth cycle of mixing resulted in further improvement of composition mixedness. Curve III (Fig. 3) was found in 8 or 9 of the 10 experiments. In these cases, a virtually molecular PA6 distribution in the LDPE matrix was observed. This phenomenon could be described as mechanical compatibilization. The studied blend started to flow at the temperature of the molecular flow of pure LDPE (about 98°C). Nevertheless it is impossible to speak about molecular flow of the blend because within the temperature range of 120–178°C only a slight reduction of the flow rate of the blend caused by some inhomogeneity was noted. A marked decrease in flow rate is apparent when the first cycle of mixing is compared with the second one. Later, the flow rate was practically constant. Four cycles of mixing do not change the structure of LDPE. The PA6 phase (Figure 3) is only transformed, and full merging of the glassy with the high-elastic states of PA6 is found. The temperature at the beginning of the flow de-

creases to 130–140°C. From the experiments described it is also concluded that even after four cycles of mixing the PA6–LDPE uniform blend behaves like a block polymer (two-phase system).

#### Mixing LDPE and 5% PA6 with 5% SEBS

On the basis of its structure, SEBS should behave as a two-phase system. Figure 4 shows the thermomechanical curves for SEBS. The figure reveals that a low-temperature phase has a  $T_g$  of –79°C. The second phase is characterized by a  $T_g$  of 30°C. SEBS starts to flow at 62°C, which is a much lower temperature than that at which polyethylene or polystyrene flows. This suggests that fractions of both these polymers joined with polybutylene create a joined phase with random distribution of components and lower temperature at the beginning of molecular flow. The pseudocrosslinked structure of a low-temperature phase is affected by the supermolecular structure of a high-temperature phase, which starts to be destroyed at about 50°C and ends at 62°C.

Using 5% SEBS accelerates the mixing of LDPE with PA6. If components are mixed by ordinary extrusion (Fig. 5) at the rate of 40 rpm, the ternary blend is inhomogeneous and has a multiphase structure. The modifier SEBS is randomly distributed in LDPE and only widens the transitional zone from a straight line of glassy expansion (point A) to a straight line of high-elastic deformation (point B). The temperatures characteristics of LDPE do not change (i.e.,  $T_e = 75^\circ\text{C}$  and  $T_m = 98^\circ\text{C}$ ). In the temperature interval of



**Figure 5** Typical thermomechanical curve of an LDPE–PA6 blend with 5% SEBS; ( $X_1$ ) zone of solid state of the blend; ( $X_2$ ) zone of high-elastic state of the blend; ( $X_3$ ) zone of molecular flow of LDPE; ( $X_4$ ) zone of PA6 in glassy and in high-elastic states; ( $X_5$ ) zone of molecular flow of PA6.  $T_m$ : melting temperature.

120–140°C in the zone of molecular flow of LDPE, rapid reduction of the flow rate is noticed owing to the deformation process when PA6 is in a nearly viscoelastic state. This process ends at a temperature of about 150°C by transition into molecular flow. From the point of view of product quality, what results is close to the state obtained when LDPE and PA6 were mixed without SEBS by 3 or 4 passes through the static mixer (Fig. 3).

In the next experiment for ternary blends, a manufacturing extruder was equipped with the static mixer. The TMC changes in the zone of LDPE flow only, and there is no visible influence of PA6. The shape of the resulting TMC is very close to that for pure LDPE. Note that practical molecular distribution of LDPE in PA6 and molecular flow of the blend start at a temperature between 96 and 102°C. The use of small amounts of SEBS widens the zone of degradation of the glassy state in the TMC from –45 to +50°C without changing the temperature at the beginning of melting and without changing homogeneity for such a blend.

## CONCLUSIONS

1. Thermomechanical measurements confirm the conclusion from previous work<sup>10</sup> that the static mixer described in this article significantly improves the homogeneity of blends of thermodynamically immiscible polymers. In some cases, it is possible to obtain very fine distribution of polymeric components through mechanical mixing.
2. The thermomechanical method of studying

polymeric structure is useful for evaluating the mixedness of LDPE with PA6 and for demonstrating the influence of their mixing conditions on the dynamics of transformation from the multiphase structure of the blend to its homogeneous, pseudomolecular distribution.

3. The block copolymer SEBS improves the effectiveness of LDPE mixing with PA6 and thus can be an effective homogenizing agent for these polymers.

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